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- 54 Method for adsorbing and decomposing ethylene and/or other odorous substances present in air or other odor-generating sources.

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Description

BACKGROUND OF THE INVENTION

The present invention relates to a method for adsorbing and decomposing ethylene and/or other odorous substances present in air or other odor-generating sources which can be utilized to maintain the freshness of postharvest vegetables, fruits and flowers by removing ethylene evolved from them or for deodorizing garbages, refrigerators, toilets, hospitals, hotels, ranches, sewage disposing plants and the like.

As plants are still alive after being harvested, various physiological effects such as respiration effect, transpiration effect, mold growth and putrefaction under the action of microorganisms, etc. may take place together and accelerate the loss of freshness of the plants. In addition, plants evolve ethylene, a kind of plant hormones, as a metabolite.

Ethylene has many physiological effects, among which there are respiratory promoting effect and maturity promoting effect, and, therefore, largely relates to maturity and also loss of freshness of the plants.

The loss of freshness has been a problem especially in the storage or the distribution of vegetables, fruits and flowers. As the postharvest preservation to maintain freshness of vegetables, fruits and flowers, the following two methods are currently employed:

(1) A method of depressing the above physiological effects by controlling the storage conditions to low temperature, reduced pressure, or low oxygen concentration; and

(2) a method of removing the evolved ethylene by an adsorbent or a catalyst.

Of the above two methods, the method (1) cannot be said to be easily accessible from the viewpoint that it requires special and complicated devices. In the method (2), the use of an adsorbent such as active carbon or zeolite, to adsorb and remove ethylene has been proposed. Such adsorbents, however, have the defects that (a) the amount of adsorption is limited due to the saturated amount of adsorption, that (b) the adsorption ability is decreased with time on use and that (c) the once adsorbed ethylene is concentrated on the surface of the adsorbent and desorbed from the surface.

Accordingly, alternate methods have been proposed, wherein catalyst component or reactive species such as potassium permanganate and potassium bromate, are carried on the adsorbent to convert adsorbed ethylene to other species. However, the thus treated adsorbents have not sufficient activity at ordinary conditions of use. It cannot be said that the defect of the adsorbent has been improved.

Other methods of utilizing oxidation activity of gaseous chlorine dioxide have been proposed. For instance, in JP-B-48-32079 (1973), a method has been disclosed wherein an aqueous solution of a chlorite is adsorbed on a basic adsorbent and stabilized, and the thus treated adsorbent is mixed with an acidic powder to generate gaseous chlorine dioxide. Furthermore, in JP-A-59-39243 (1984), a composition which is able to generate gaseous chlorine dioxide has been disclosed, wherein it is prepared by impregnating a porous inorganic carrier with an aqueous solution of a chlorite adjusted to pH 9 to 14.

However, the method of using gaseous chlorine dioxide may not be practical. Because it is difficult to control the amount of generation of the gas and also to prevent its decomposition during storage of itself. Moreover, the activity no more exists when all chlorite on the carrier is decomposed. Besides, there are some cases where the generation of chlorine dioxide is undesirable in consideration of the environmental pollution.

In addition to these, even if ethylene can be removed by the use of above ethylene removal agents, sufficient postharvest preservation will not be expected. It is difficult for them to inhibit the growth of mold and putrefaction.

There are also many varieties of sources of generation of offensive odors, such as garbages in daily life, refrigerators, factories, ranches, sewage disposing plants, etc. Besides, there are many places having odor not offensive but characteristic, such as hospitals, hotels and restaurants.

As the substances which cause these offensive odors, ammonia, mercaptans, sulfides, amines and aldehydes have attracted the attention. However, the actual situation is more complicated and the causes of offensive odors are not limited to the above substances.

In recent years, many researches for removing the offensive odors have been performed with the raise of the demand for the methods of removing these offensive odors. Typical methods now available are summarized as follows:

(1) The masking method by using aromatic substances of pleasant smell to mask that of foul-smelling substances;

(2) the adsorption method of adsorbing the foul-smelling substances by using adsorbents such as active carbon;

(3) the acid-base neutralization method of neutralizing the foul-smelling substances with acids or bases;

(4) the chemical oxidation or reduction method of chemically decomposing the foul-smelling substances.

However, each method listed above has serious defects. The masking method cannot be said to be a substantial method. The adsorption method has a limit of the amount of adsorption due to the saturated amount of adsorption and is not effective against strong offensive odors. The acid-base neutralization method is limited to the substances which can be neutralized and, therefore, the odors which can be removed are limited.

The chemical oxidation-reduction method is considered to be the most expected technique, though any method having a sufficient activity has not yet been found. Of the chemical oxidation-reduction methods, several techniques of utilizing the oxidation activity of gaseous chlorine dioxide have been proposed.

For instance, in JP-B-48-32079 (1973), a method has been disclosed, wherein an aqueous solution of a chlorite is adsorbed to a basic adsorbent and stabilized, and the thus treated adsorbent is mixed with an acidic powder to generate gaseous chlorine dioxide. Furthermore, in JP-A-60-161307 (1985), a composition which is able to generate gaseous chlorine dioxide has been disclosed, wherein it is prepared by impregnating a porous inorganic carrier with an aqueous solution of a chlorite.

However, the method of using gaseous chlorine dioxide is not practical. Because it is difficult to control the amount of generation of the gas and also to prevent its decomposition during the storage of itself. Moreover, the activity no more exists when all chlorite on the carrier is decomposed. Besides, there are some cases where the generation of chlorine dioxide is undesirable in consideration of the environmental pollution.

Although each of the above methods has a deodorizing effect to some extent and is actually applied, the technical improvement of the methods has been strongly demanded from the view point of the above defects.

In FR-A-2 411 625 there is disclosed an agent and a method for deodorising a gas which comprises odorous substances or for deodorizing an odor-generating source by contacting said gas or said source with said agent consisting of a protonic acid, a Lewis-acid and an acid salt provided on a support in an amount of 1 to 50 % by weight of the support. As protonic acid phosphoric acid can be used, as Lewis-acid nickel sulfate can be used and as acid salt the reaction product between the protonic acid and a foul-smelling substance can be used. The support consists of silica or silica-alumina.

From DE-A-27 00 450 an oxidation solution is known comprising an oxidizing agent and vanadium pentoxide. The oxidizing agent can be an alkali metal chlorate or a peroxide. This known oxidizing solution can be used to oxidize gaseous hydrocarbons like ethylene, propylene and the like.

However, in both cases the technical effect which can be achieved in regard to the removal of ethylene and/or other odorous substances present in air or other odor-generating sources is no more sufficient.

Therefore, it is an object of the present invention to provide a novel means for adsorbing and decomposing ethylene and/or other odorous substances present in air or other odor-generating sources which do not have the above defects of the conventional methods.

In consideration of this background, the present inventors have investigated a highly active and stable ethylene removal agent which adsorbs and decomposes ethylene and a postharvest preservation agent which maintains freshness of vegetables, fruits and flowers and have also investigated a highly active deodorant which adsorbs and decomposes various kinds of bad odors of garbages, refrigerators, toilets, ranches, refuse disposing plants, sewage disposing plants, etc.

As a result of the investigation, the present inventors have found that this object of the invention can be achieved by using a composition prepared by adding a specified compound in a specific amount to at least one compound selected from the group consisting of phosphoric acid, phosphorous acid, hypophosphorous acid, the salts of these acids and hypochlorite, which has a high activity of decomposing ethylene and foul-smelling substances, and a stable deodorization effect which can be attained which have not been hitherto known. On the basis of these findings, the present inventors have accomplished the present invention.

SUMMARY OF THE INVENTION

Subject-matter of the present invention is a method for adsorbing and decomposing ethylene and/or other odorous substances present in air or other odor-generating sources, which method comprises placing in proximity to said source a composition which comprises

(A) at least one compound selected from the group consisting of phosphoric acid, phosphorous acid, hypophosphorous acid, salts of said acids and hypochlorite and

(B) at least one compound selected from the group consisting of oxides and peroxides of iron, cobalt, titanium, copper, zinc, magnesium, calcium, and barium, the weight ratio of the component (A) to the component (B) being in the range of 1 : 0,001-99.

According to one aspect the present invention relates to a method for removing ethylene from an ethylene-generating source, which method comprises placing in proximity to said source a composition which comprises

(A) at least one compound selected from the group consisting of phosphoric acid, phosphorous acid, hypophosphorous acid, salts of said acids and hypochlorite and

(B) at least one compound selected from the group consisting of oxides and peroxides of cobalt, titanium, copper, zinc, magnesium, calcium and barium, and Fe_2O_3 ,

the weight ratio of the component (A) to the component (B) being in the range of 1 : 0,001-99.

According to a further aspect the present invention relates to a method for preserving harvested fruits, vegetables or flowers,

which method comprises placing in proximity to said fruits, vegetables or flowers a composition which comprises

(A) at least one compound selected from the group consisting of phosphoric acid, phosphorous acid, hypophosphorous acid, salts of said acids and hypochlorite and

(B) at least one compound selected from the group consisting of oxides and peroxides of cobalt, titanium, copper, zinc, magnesium, calcium and barium, and Fe_2O_3 ,

the weight ratio of the component (A) to the component (B) being in the range of 1 : 0,001-99.

According to another aspect the present invention relates to a method for deodorizing a gas which comprises odorous substances,

which method comprises bringing said gas into contact with a composition which comprises

(A) at least one compound selected from the group consisting of phosphoric acid, phosphorous acid, hypophosphorous acid and hypochlorite and

(B) at least one compound selected from the group consisting of oxides and peroxides of iron, titanium, copper, zinc, magnesium, calcium and barium,

the weight ratio of the component (A) to the component (B) being in the range of 1 : 0,001-99.

According to a further aspect the present invention relates to a method for deodorizing an odor-generating source,

which method comprises adding to said source a composition which comprises

(A) at least one compound selected from the group consisting of phosphoric acid, phosphorous acid, hypophosphorous acid and hypochlorite and

(B) at least one compound selected from the group consisting of oxides and peroxides of iron, titanium, copper, zinc, magnesium, calcium and barium,

the weight ratio of the component (A) to the component (B) being in the range of 1 : 1,001-99.

Preferred embodiments of the present invention are described in subclaims 6 to 17.

DETAILED DESCRIPTION OF THE INVENTION

The present invention relates to the use of an ethylene removal agent, a postharvest preservation agent and a deodorant comprising

(A) at least one compound selected from the group consisting of phosphoric acid, phosphorous acid, hypophosphorous acid, salts of these acids and hypochlorite and

(B) at least one compound selected from the group consisting of oxides and peroxides of iron, cobalt, titanium, copper, Zinc, magnesium, calcium and barium.

The characteristics of the ethylene removal agent, the postharvest preservation agent and the deodorant used according to the present invention are in

1) the evolution of no gas like chlorine dioxide during the use thereof,

2) the high activity in adsorbing and decomposing ethylene and foul-smelling substances and

3) the stable activity during the use or the storage for a long period. These are the characteristics which the present inventors aimed to achieve. However, it has been found that the materials used according to the present invention have additional unexpected characteristics, as follows:

4) It decomposes gases other than ethylene such as ethyl alcohol and acetaldehyde evolved from vegetables, fruits and flowers. These gases are also considered to effect on the postharvest preservation.

5) It inhibits the growth of mold and putrefaction.

6) It decomposes ethylene and foul-smelling substances more effectively under the circumstances of high humidity. Storage conditions of vegetables, fruits and flowers and foul-smelling places are usually humid.

Phosphoric acid, phosphorous acid, hypophosphorous acid, salts thereof and hypochlorite used in the invention (hereinafter referred to as "the component (A)") include the acids having different degree of

hydration (ortho acid, meta acid, polyacid, etc.), the acidic salts and the normal salts of the acids.

As the salts of phosphoric acid, phosphorous acids, hypophosphorous acid and hypochlorous acid, sodium salt, potassium salt, magnesium salt, calcium salt, barium salt, strontium salt, iron salt, cobalt salt, nickel salt, copper salt, zinc salt, zirconium salt, manganese salt, and lead salt, may be included.

5 The preferred components (A) are hypophosphorous acid, salts thereof and hypochlorites. Sodium salt, potassium salt, magnesium salt, calcium salt and iron salt are preferable as the salts.

Components (B) include oxides and peroxides of iron, cobalt, copper, zinc, magnesium, calcium and barium.

10 Of the components (B), those more preferable are oxides or peroxides of iron, titanium, copper, zinc, magnesium, calcium and barium. Of these compounds, oxides and peroxides of iron, titanium, zinc, magnesium and calcium are particularly preferable.

In this case where at least one of phosphoric acid, phosphorous acid, hypophosphorous acid and the salts thereof is contained as one of the components, it is preferred that at least one of peroxides is added as one of the other components.

15 The component (A) and the component (B) are used in the ratio of component (A) : component (B) = 1 : 0,001-99 (by weight). The preferable ratio for use is component (A) : component (B) = 1 : 0,001-30 (by weight), and particularly preferable ratio for use is component (A) : component (B) = 1 : 0,001-10 (by weight).

20 The ethylene removal agent, the postharvest preservation agent and the deodorant used according to the present invention can contain other active components than the components (A) and (B). As such components, for instance, chloric acid, chlorous acid and salts thereof may be employed. As the salts of chloric acid and chlorous acid, sodium salt, potassium salt, magnesium salt, calcium salt, barium salt and strontium salt may be included. These active components may be employed in the preferable ratio of 0 to 50 % by weight to the amount of the component (A), and more preferably in the ratio of 0 to 30 % by weight.

25 The ethylene removal agent, the postharvest preservation agent and the deodorant used according to the present invention can also be carried on a porous carrier. Any carrier may be used; however, the preferred carriers are silica, alumina, silicaalumina, natural zeolite, synthetic zeolite, diatomaceous earth, active carbon, clays, and Kanuma earth. The carrier can comprise about 10 to 90 % by weight of the total composition including the carrier itself, and more preferably 30 to 90 % by weight of the total composition.

30 The raw materials and the method of preparation of the ethylene removal agent, the postharvest preservation agent and the deodorant used according to the present invention are not particularly limited. As phosphoric acid, phosphorous acid, hypophosphorous acid, the salts thereof and hypochlorite those ordinarily available may be used. As oxides and peroxides of iron, cobalt, titanium, copper, zinc, magnesium, calcium and barium reagents available can be used as they are. Alternatley, oxides may be made by calcining nitrates or hydroxides.

35 The ethylene removal agent, the postharvest preservation agent and the deodorant used according to the present invention may be prepared by, for instance, merely mixing mechanically all the components. Or after preparing the mixture of the components (B) and the carrier, if necessary, by suitable reaction or mechanical mixing, at least one of the components (A) may be mixed mechanically or impregnated from the solution.

40 The thus obtained ethylene removal agent and postharvest preservation agent may be used by any suitable method. For instance, each of these agents is molded into a form of pellets and is used in a bag or a vessel having suitable gas permeability. Further, it is possible to mix these agents with filmforming materials such as polyethylene to form into films, or to apply these agents into packaging materials like papers.

45 The deodorant used according to the present invention may be used by any suitable method. For instance, after molding the deodorant into a form of granules or pellets, it is packed into a bag or a vessel having suitable gas permeability. The thus packed deodorant can be used in refrigerators and toilets. It may be possible to pass foul-smelling gasses through the layer of the deodorant of the present invention, thereby removing the odors. It may be possible to add the deodorant directly into the source of bad odors such as sewage and garbages. Moreover, it may also be possible to apply the deodorant onto or to mix the deodorant with house-building materials such as packaging materials, and wallpapers.

50 The ethylene removal agent and the postharvest preservation agent used according to the present invention have characteristics of decomposing low concentration of gaseous ethylene and also of keeping freshness of vegetables, fruits and flowers. This function of postharvest preservation may be due not only to its high activity of decomposing ethylene, but it has additional abilities to decompose other gases evolved and to inhibit the growth of mold and putrefaction.

Although the mechanism of decomposing ethylene by the ethylene removal agent used according to the present invention has not been elucidated, it is considered that it may be due mainly to catalysis. Ethylene is decomposed into carbon dioxide and the like. Therefore, different from the adsorbents and the chlorine dioxide generating agents, the ethylene removal agent and the postharvest preservation agent used according to the present invention can be used for a longer time period. Besides, since they have higher activity, there is a merit that a small amount thereof is enough for use. The conditions for their use are not limited. The agents sufficiently exhibit their ability even in the atmosphere controlled at low temperature of e.g. 0 °C, under high humidity or under low concentration of oxygen.

The deodorant used according to the present invention adsorbs and converts foul-smelling substances such as ammonia, mercaptans, sulfides, amines, and aldehydes into odorless substances. Although its mechanism has not yet been elucidated, it is considered that it may be due mainly to catalysis. Accordingly, different from the adsorbents and the chlorine dioxide generating agents, the deodorant used according to the present invention can be used for a longer period. Furthermore, since it has higher activity, it has a merit that effectiveness thereof is exhibited within a short period of time. And it can be applied to the treatment of the odors of extremely high concentrations. Accordingly, the deodorant used according to the present invention can be utilized broadly as a deodorant.

As described above, the ethylene removal agent used according to the present invention is able to decompose and remove ethylene effectively present in air or other atmosphere in low concentration and is possible to be used for a long period of time without losing its activity. Therefore, it is useful as the postharvest preservation agent.

The ethylene removal agents obtained in examples can be naturally used, as they are, as the postharvest preservation agents.

The present invention will be explained more precisely while referring to the following examples.

EXAMPLE 1:

In the presence of a small amount of water, 25 g of hypophosphorous acid, 25 g of ferric oxide and 50 g of granular silica-alumina (containing 25 % by weight of alumina) were kneaded to mix uniformly, and after drying the thus obtained mixture at 110 °C, the solid material obtained was pulverised into a powder 1.0 to 0.70 mm (16 to 24 meshes).

1 g of the material prepared above was placed into a vessel of a capacity of 130 ml and 20 µl of gaseous ethylene were introduced into the vessel (corresponding to about 150 ppm of ethylene). Thereafter, the change of the concentration of ethylene in the vessel at room temperature was measured by an FID gaschromatograph. The results are shown in Table 1.

EXAMPLES 2 to 4:

In the same manner as in Example 1, the materials having the compositions shown in Table 1 were obtained. The change of the concentration of ethylene with time was measured as in Example 1. The results are also shown in Table 1.

EXAMPLES 5 to 6:

In the same manner as in Example 1, the materials having the compositions shown in Table 2 were obtained. The change of the concentration of ethylene with time was measured for each material as in Example 1. The results are shown in Table 2.

TABLE 1

| Example | Composition | Concentration of ethylene(ppm) after | | | | |
|---------|--|--------------------------------------|--------|--------|---------|--------|
| | | 10 min | 20 min | 30 min | 60 min. | 90 min |
| 1 | H ₃ PO ₂ /Fe ₂ O ₃ /silica-alumina | 55 | 25 | 11 | 0 | 0 |
| 2 | H ₃ PO ₂ /CoO /silica-alumina | 65 | 29 | 14 | 0 | 0 |
| 3 | H ₃ PO ₂ /TiO ₂ /active carbon | 57 | 22 | 12 | 0 | 0 |
| 4 | H ₃ PO ₂ /CuO /silica-alumina | 78 | 33 | 21 | 5 | 0 |

TABLE 2

| Example | Composition | Concentration of ethylene (ppm) after | | | | |
|---------|-------------------------------|---------------------------------------|--------|--------|--------|--------|
| | | 10 min | 20 min | 30 min | 60 min | 90 min |
| 5 | H_3PO_2/ZnO /silica-alumina | 50 | 21 | 8 | 0 | 0 |
| 6 | H_3PO_2/HgO /silica-alumina | 59 | 25 | 10 | 0 | 0 |

EXAMPLES 7:

In the presence of a small amount of water, 20 g of hypophosphorous acid, 10 g of ferric oxide, 10 g of zinc oxide, 20 g of calcium oxide and 40 g of granular silica-alumina (containing 28 % by weight of alumina)

were kneaded to mix uniformly, and after drying the mixture at 110 °C, the material obtained was pulverized into a powder of 1,0 to 0,70 mm to (16 to 24 meshes).

The change of the concentration of ethylene with time was measured for the material prepared above in the same manner as in Example 1 and the results are shown in Table 3.

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EXAMPLES 8 and 9:

In the same manner as in Example 7 except that phosphorous acid (Example 8) and phosphoric acid (Example 9) were used respectively instead of hypophosphorous acid, the materials having the compositions shown in Table 3 were obtained.

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The change of the concentration of ethylene with time was measured for each material as in Example 1. The results are also shown in Table 3. As will be seen in Table 3, almost same results were obtained by using phosphorous acid or phosphoric acid instead of hypophosphorous acid.

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EXAMPLES 10 to 12:

In the same manner as in Example 7, the materials having the compositions shown in Table 3 were obtained, and the change of the concentration of ethylene with time was measured for each material in the same manner as in Example 1. The results are also shown in Table 3.

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EXAMPLE :13;

In the same manner as in Example 1 to 6 except that phosphoric acid, phosphorous acid, sodium phosphate, sodium phosphite, or sodium hypophosphite was used instead of hypophosphorous acid in Examples 1 to 6, the corresponding materials were obtained. The change of the concentration of ethylene with time was measured for each material. Almost same results were obtained as those of Examples 1 to 6.

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TABLE 3

| Example | Composition | Concentration of ethylene (ppm) after | | | | |
|---------|---|---------------------------------------|--------|--------|--------|--------|
| | | 10 min | 20 min | 30 min | 60 min | 90 min |
| 7 | $H_3PO_2/Fe_2O_3/ZnO/CaO/silica-alumina$ | 31 | 10 | 0 | 0 | 0 |
| 8 | $H_3PO_3/Fe_2O_3/ZnO/CaO/silica-alumina$ | 45 | 14 | 5 | 0 | 0 |
| 9 | $H_3PO_4/Fe_2O_3/ZnO/CaO/silica-alumina$ | 40 | 11 | 2 | 0 | 0 |
| 10 | $Na_3PO_2/Fe_2O_3/ZnO/CaO/silica-alumina$ | 50 | 16 | 7 | 0 | 0 |
| 11 | $FePO_4/Fe_2O_3/ZnO/CaO/silica-alumina$ | 46 | 12 | 3 | 0 | 0 |
| 12 | $MgHPO_4/Fe_2O_3/ZnO/CaO/silica-alumina$ | 42 | 12 | 4 | 0 | 0 |

EXAMPLE 14:

Example 7 was repeated except that the amount of gaseous ethylene was increased to 0.26 ml (the initial concentration of ethylene in a vessel was about 2000 ppm). It was found that ethylene could not be

detected after 90 minutes.

EXAMPLE :15:

5 In the presence of a small amount of water, 25 g of calcium hypochlorite, 25 g of ferrous oxide and 50 g of granular silicaalumina (containing 28 % by weight of alumina) were kneaded to mix uniformly, and after drying the mixture at 110 °C, the thus obtained solid material was pulverized into powder of 1,0 to 0,70mm (16 to 24 meshes).

10 1 g of the material prepared above was placed into a vessel of a capacity of 230 ml, and 0.46 ml of gaseous ethylene was introduced into the vessel (corresponding to about 2000 ppm of ethylene). Then, the change of the concentration of ethylene with time was measured by an FID gaschromatograph. The results are shown in Table 4.

EXAMPLES 16 to 18:

15 In the same manner as in Example 15, the materials having the composition shown in Table 4, were obtained. The change of the concentration of ethylene with time was measured for each material prepared above in the same manner as in Example 15. The results are shown also in Table 4.

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Table 4

| Example | Composition | Concentration of ethylene (ppm) after | | | | |
|---------|--|---------------------------------------|--------|---------|---------|----------|
| | | 0.5 hours | 1 hour | 2 hours | 5 hours | 24 hours |
| 15 | Ca(ClO) ₂ /FeO/silica-alumina | 21 | 3 | 0 | 0 | 0 |
| 16 | Ca(ClO) ₂ /CoO/silica-alumina | 18 | 5 | 0 | 0 | 0 |
| 17 | Ca(ClO) ₂ /TiO ₂ /silica-alumina | 35 | 10 | 3 | 0 | 0 |
| 18 | NaClO/CuO/active carbon | 50 | 15 | 2 | 0 | 0 |

EXAMPLE 19;

In the presence of a small amount of water, 20 g of calcium hypochlorite, 20 g of ferrous oxide, 10 g of zinc oxide and 50 g of granular silica-alumina (containing 28 % by weight of alumina) were kneaded to mix

uniformly, and after drying the mixture at 110 °C, the thus obtained solid material was pulverized into powder of 1,0 to 0,70 mm (16 to 24 meshes).

The ethylene removal activity of the material prepared above was measured in the same manner as in Example 15 and the results are shown in Table 5.

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EXAMPLES 20 and 21:

In the same manner as in Example 19, the materials having the composition shown in Table 5 were obtained. The change of the concentration of ethylene with time was measured for each material in the same manner as in Example 15. The results are also shown in Table 5.

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Table 5

| Example | Composition | Concentration of ethylene (ppm) after | | | | | |
|---------|---|---------------------------------------|--------|---------|---------|----------|--|
| | | 0.5 hours | 1 hour | 2 hours | 5 hours | 24 hours | |
| 19 | Ca(ClO) ₂ /FeO/ZnO/silica-alumina | 15 | 2 | 0 | 0 | 0 | |
| 20 | Ca(ClO) ₂ /FeO/GeO ₂ /silica-acti-alumina | 13 | 2 | 0 | 0 | 0 | |
| 21 | Ca(ClO) ₂ /TiO ₂ /Fe ₂ O ₃ /ve carbon | 10 | 1 | 0 | 0 | 0 | |

In Table 5 the composition ratio is 20/20/10/50 (by weight).

EXAMPLE 22;

In the presence of a small amount of water, 25 g of calcium hypochlorite, 25 g of barium oxide and 50 g of granular silicaalumina (containing 28 % by weight of alumina) were kneaded to mix uniformly, and after

drying the mixture at 110°C, the thus obtained solid material was pulverized into powder of 1,0 to 0,70mm (16 to 24 meshes).

1 g of the material prepared above was placed into a vessel of a capacity of 230 ml and 0.46 ml of gaseous ethylene was introduced into the vessel (the concentration of ethylene in the vessel was about 2000 ppm). The change of the concentration of ethylene with time at room temperature was measured. The results are shown in Table 6.

EXAMPLES 23 to 25:

In the same manner as in Example 22 except that magnesium oxide (Example 23), calcium oxide (Example 24), and zinc oxide (Example 25) were used instead of barium oxide in Example 22, the materials shown in Table 6 were obtained, respectively.

The change of the concentration of ethylene with time was measured for each material. The results are shown in Table 6.

EXAMPLE 26:

136.4 g of barium nitrate and 146.2 g of zinc nitrate were dissolved into 800 ml of water, where 200 g of granular silicaalumina were added. After evaporating the above solution to dryness under agitation, the solid material obtained was pulverized into a powder of 1,0 to 0,70 mm (16 to 24 meshes) and calcined for 4 hours at 500 C. The composition of the powder obtained was BaO : ZnO : silica-alumina = 20 : 10: 50 (by weight).

200 ml of 10 % calcium hypochlorite aqueous solution were added to 80g of the thus obtained powder, which was evaporated to dryness under agitation and dried at 110°C.

The change of the concentration of ethylene with time was measured in the same manner as in Example 22. As a result, the concentration of ethylene, which was initially about 2000 ppm, was changed to almost zero after 2 hours and remained zero even after 24 hours.

Thereafter, 0.46 ml of ethylene was repeatedly introduced into the vessel every 24 hours, and the change of the concentration of ethylene with time was measured. The results are shown in Table 7. As is seen in the table, the activity was maintained for a long period of time.

Table 6

| Example | Composition | Concentration of ethylene (ppm) after | | | | |
|---------|--|---------------------------------------|---------|---------|---------|----------|
| | | 1 hour | 3 hours | 5 hours | 8 hours | 24 hours |
| 22 | Ca(ClO) ₂ /BaO/silica-alumina | 25 | 8 | 0 | 0 | 0 |
| 23 | Ca(ClO) ₂ /MgO/silica-alumina | 32 | 5 | 0 | 0 | 0 |
| 24 | Ca(ClO) ₂ /CaO/silica-alumina | 20 | 3 | 0 | 0 | 0 |
| 25 | Ca(ClO) ₂ /ZnO/silica-alumina | 20 | 4.1 | 0 | 0 | 0 |

Table 7

| Operation | Concentration of ethylene (ppm) after | | | | |
|--|---------------------------------------|---------|---------|---------|----------|
| | 1 hour | 3 hours | 5 hours | 8 hours | 24 hours |
| Introducing ethylene to a concentration of 2000 ppm | 2 | 0 | 0 | 0 | 0 |
| Introducing ethylene to a concentration of 2000 ppm after 24 hours | 5 | 0.5 | 0 | 0 | 0 |
| Introducing ethylene to a concentration of 2000 ppm after 48 hours | 4 | 0.7 | 0 | 0 | 0 |

55 EXAMPLE 27

In the same manner as in Example 26, the materials having the compositions shown in Table 8 were prepared, respectively. The change of the concentration of ethylene with time was measured for each

material. The results are shown in Table 8.

Table 8

| Example | Composition | Concentration of ethylene (ppm) after | | | | |
|---------|---|---------------------------------------|---------|---------|---------|----------|
| | | 1 hour | 3 hours | 5 hours | 8 hours | 24 hours |
| 27 | $\text{Ba}(\text{ClO})_2/\text{CaO}/\text{ZnO}/\text{NaY}$ zeolite | 3 | 0.2 | 0 | 0 | 0 |

EXAMPLE 28:

In the presence of a small amount of water, 15 g of calcium hypochlorite, 10 g of sodium chlorite, 25 g of titanium oxide and 150 g of active carbon powder were kneaded to mix uniformly, and the mixture obtained was dried at 110°C.

The change of the concentration of ethylene with time was measured for the material obtained above. The results are shown in Table 9.

Table 9

| Example | Composition | Concentration of ethylene (ppm) after | | | | |
|---------|---|---------------------------------------|--------|---------|---------|----------|
| | | 30 min. | 1 hour | 2 hours | 5 hours | 24 hours |
| 28 | $\text{Ca}(\text{ClO})_2/\text{NaClO}_2/\text{TiO}_2/$ active carbon | 28 | 8 | 0 | 0 | 0 |

EXAMPLE 29:

50 g of 50 % hypophosphorous acid aqueous solution were added to 50 g of active carbon powder, and after mixing, 25 g of calcium peroxide were further added. After mixing uniformly, the mixture was dried at 110°C.

The change of the concentration of ethylene with time was measured for the material obtained above in the same manner as in Example 1. The results are shown in Table 10.

EXAMPLES 30 and 31:

In the same manner as in Example 29 except that 50 % phosphorous acid aqueous solution (Example 30) and 50 % phosphoric acid aqueous solution (Example 31) were used instead of 50 % hypophosphorous acid aqueous solution, two kinds of the materials shown in Table 10 were obtained, respectively. The change of the concentration of ethylene with time was measured for each material in the same manner as in Example 1. The results are shown in Table 10:

EXAMPLE 32:

20 g of 50 % hypophosphorous acid aqueous solution were added to 40 g of active carbon powder and mixed, followed by adding 20 g of zinc oxide and 20 g of calcium peroxide and mixing uniformly. The mixture was dried at 110°C.

The change of the concentration of ethylene with time was measured for the material obtained above in the same manner in Example 1. The results are also shown in Table 10.

EXAMPLES 33 and 34

In the same manner as in Example 32, the materials having the compositions shown in Table 10 were obtained and the change of the concentration of ethylene with time was measured for each material. The results are also shown in Table 10.

EXAMPLE 35:

Each of 1 kg of green tangerine, 1 kg of peach and 1 kg of broccoli was sealed in a polyethylene bag of 0.03 mm thickness together with 2 g of the material prepared in Example 19, respectively and stored at room temperature in order to evaluate the ability as the postharvest preservation agent. The results are shown in Table 11 together with the results of the control without the agent.

Table 10

| Example | Composition | Concentration of ethylene (ppm) after | | | | |
|---------|---|---------------------------------------|--------|--------|--------|--------|
| | | 10 min | 20 min | 30 min | 60 min | 90 min |
| 29 | H ₃ PO ₂ /CaO ₂ /active carbon | 32 | 14 | 4 | 0 | 0 |
| 30 | H ₃ PO ₃ /CaO ₂ /active carbon | 40 | 16 | 8 | 0 | 0 |
| 31 | H ₃ PO ₄ /CaO ₂ /active carbon | 36 | 13 | 5 | 0 | 0 |
| 32 | H ₃ PO ₂ /CaO ₂ /ZnO/active carbon | 20 | 7 | 0 | 0 | 0 |
| 33 | H ₃ PO ₂ /CaO ₂ /TiO ₂ /zeolite | 17 | 6 | 0 | 0 | 0 |
| 34 | FePO ₄ /BaO ₂ /active carbon | 39 | 15 | 5 | 0 | 0 |

Table 11

| Days of storage | Green tangerine | | Peach | | Brocoli | |
|-----------------|-------------------|---------------|--------------------------|-----------|---------------------|-------------------|
| | Control | Used | Control | Used | Control | Used |
| 1 | no change | no change | no change | no change | no change | no change |
| 2 | no change | no change | no change | no change | slightly yellowed | no change |
| 3 | no change | no change | partly changed in colour | no change | yellowed | no change |
| 4 | slightly yellowed | no change | brown spots | no change | completely yellowed | no change |
| 5 | slightly yellowed | no change | began to rot | no change | began to mold | no change |
| 6 | yellowed | no change | completely rotten | no change | rotten | slightly yellowed |
| 7 | yellowed | no change | - | dark red | - | - |
| 8 | partly rotten | no change | - | dark red | - | - |
| 30 | partly rotten | half yellowed | - | - | - | - |

EXAMPLES 36 to 39:

Three kiwi fruits were sealed in each polyethylene bag of 0.03 mm thickness together with 1 g of each of the materials prepared in Examples 19, 21, 28 and 33 and stored at room temperature. The results were compared with those of the control in which the above materials were not used. The fruits of the control were completely softened after 30 days, while the fruits stored in each bag with each material maintained the initial hardness even after 30 days.

EXAMPLES 40 to 42:

Two apples were sealed in a polyethylene bag of 0.03 mm thickness together with 1 g of each of the materials prepared in Examples 7, 21 and 33 and stored at room temperature. The results were compared with those of the control in which the above materials were not used. As the results, the upper part of the apples of the control were changed into brown in colour and began to get out the shape after 30 days, while the apples stored with the above materials remained unchanged in the shape and the taste.

EXAMPLES 43 and 44:

In a polyethylene bag of 0.03 mm thickness were sealed 200 g of white mushroom together with 1 g of each of the materials prepared in Examples 19 and 33 and stored at room temperature, which were compared with the control.

As the results, the white mushrooms of the control changed into brown in colour on the 2nd day, while those stored with the above materials remained unchanged in colour even after 4 days. In addition, ethyl alcohol was detected in the former, but not in the latter, which suggests that ethyl alcohol was decomposed by the materials used.

EXAMPLE 45:

A block of broccoli was sealed in a polyethylene bag together with 1 g of the material prepared in Example 7 and stored at room temperature, which was compared with the control.

As the results, the broccoli of the control changed completely into yellow on the 4th day and began to rot on the 6th day, while the broccoli stored with the material kept the initial green colour after 6 days.

EXAMPLE 46 to 48:

1 kg of cherries was packed in a corrugated carton with 5 g of the material prepared in Examples 19, 21 and 32, respectively and stored at room temperature.

As the results, all of them kept unchanged after 7 days, while cherries of the control were partly turned black and the mold was observed on a part of cherries after 3 days.

EXAMPLE A-1:

In the presence of a small amount of water, 25 g of hypophosphorous acid, 25 g of ferric oxide and 50 g of granular silica-alumina (containing 28 % by weight of alumina) were kneaded to mix uniformly, and after drying the thus obtained mixture at 110 C, the solid material obtained was pulverized into powder of 1,0 to 0,70 mm (16 to 24 meshes) to obtain a deodorant.

After sealing 1 g of the thus obtained deodorant in a polyethylene vessel together with 500 ml of a sample gas containing 1000 ppm of methylmercaptan, 500 ppm of hydrogen sulfide and 500 ppm of ammonia, the concentration of each component of the gas in the vessel was measured by gaschromatography. The results are shown in Table A-1.

EXAMPLES A-2 to A-4:

In the same manner as in Example A-1, the deodorants having the compositions shown in Table A-1 were obtained, respectively. The activity of each of the deodorants was measured in the same manner as in Example A-1 and the results are shown in Table A-1.

EXAMPLES A-5 to A-6:

In the same manner as in Example A-1, the deodorants having the compositions shown in Table A-2 were obtained, respectively. The activity of each of the deodorants was measured in the same manner as in Example A-1 and the results are shown in Table A-2.

EXAMPLE A-7:

In the presence of a small amount of water, 20 g of hypophosphorous acid, 20 g of zinc oxide, 20 g of calcium peroxide and 40 g of active carbon powder were kneaded to mix uniformly, and after drying the mixture obtained at 110 °C, the solid material obtained was pulverized to powder of 1,0 to 0,70 mm 16 to 24 meshes to obtain a deodorant.

The activity of the deodorant was measured in the same manner as in Example A-1 and the results are shown in Table A-3.

EXAMPLES A-8 and A-9:

In the same manner as in Example A-7 except that phosphorous acid (Example A-8) and phosphoric acid (Example A-9) are used instead of hypophosphorous acid, the deodorants having the compositions shown in Table A-3 were obtained, respectively. The activity of each of the deodorants was measured in the same manner as in Example A-1 and the results are shown in Table A-3.

As is clearly seen in the table, almost the same results were obtained by using phosphorous acid or phosphoric acid instead of hypophosphorous acid.

EXAMPLES A-10 to A-13:

In the same manner as in Example A-7, the deodorants having the compositions shown in Table A-3 were obtained, respectively and the activity of each of the deodorants was measured in the same manner as in Example A-1. The results are also shown in Table A-3.

Table A-1

| Example | Composition | Substance | Concentration (ppm) after | | |
|---------|--------------------------------------|------------------|---------------------------|--------|---------|
| | | | 30 min | 1 hour | 2 hours |
| A-1 | $H_3PO_2/Fe_2O_3/silica-$ alumina | methylmercaptan | 20 | 0 | 0 |
| | | hydrogen sulfide | 15 | 0 | 0 |
| | | ammonia | 32 | 5 | 0 |
| A-2 | $H_3PO_2/CoO/silica-$ alumina | methylmercaptan | 25 | 0 | 0 |
| | | hydrogen sulfide | 11 | 0 | 0 |
| | | ammonia | 25 | 2 | 0 |
| A-3 | $H_3PO_2/TiO_2/active$ carbon | methylmercaptan | 29 | 0 | 0 |
| | | hydrogen sulfide | 22 | 1 | 0 |
| | | ammonia | 34 | 5 | 0 |
| A-4 | $H_3PO_2/CuO/active$ carbon | methylmercaptan | 37 | 5 | 0 |
| | | hydrogen sulfide | 20 | 0 | 0 |
| | | ammonia | 30 | 5 | 0 |

Table A-2

| Example | Composition | Substance | Concentration (ppm) after | | |
|---------|--|--|---------------------------|--------|---------|
| | | | 30 min | 1 hour | 2 hours |
| A-5 | H ₃ PO ₂ /ZnO/Silica-alumina | methylmercaptan hydrogen sulfide ammonia | 22 | 0 | 0 |
| | | | 15 | 0 | 0 |
| | | | 18 | 0 | 0 |
| A-6 | H ₃ PO ₂ /MgO/Silica-alumina | methylmercaptan hydrogen sulfide ammonia | 26 | 2 | 0 |
| | | | 15 | 0 | 0 |
| | | | 21 | 5 | 0 |

Table A-3

| Example | Composition | Substance | Concentration (ppm) after | | |
|---------|---------------------------------------|--|---------------------------|--------------|-------------|
| | | | 15 min. | 30 min. | 60 min. |
| A-7 | $H_3PO_2/ZnO/CaO_2$ / active carbon | methylmercaptan hydrogen sulfide ammonia | 10 5 25 | 0 0 5 | 0 0 0 |
| A-8 | $H_3PO_3/ZnO/CaO_2$ / active carbon | methylmercaptan hydrogen sulfide ammonia | 12 6 27 | 0 0 8 | 0 0 0 |
| A-9 | $H_3PO_4/ZnO/CaO_2$ / active carbon | methylmercaptan hydrogen sulfide ammonia | 12 5 25 | 0 0 8 | 0 0 0 |
| A-10 | $Na_3PO_2/ZnO/CaO_2$ / active carbon | methylmercaptan hydrogen sulfide ammonia | 25 12 30 | 5 0 10 | 0 0 0 |
| A-11 | $FePO_4/ZnO/CaO_2$ / active carbon | methylmercaptan hydrogen sulfide ammonia | 28 15 32 | 8 0 11 | 0 0 0 |
| A-12 | $MgHPO_4/ZnO/CaO_2$ / active carbon | methylmercaptan hydrogen sulfide ammonia | 25 15 28 | 3 0 9 | 0 0 0 |
| A-13 | $H_3PO_2/CaO_2/TiO_2$ / active carbon | methylmercaptan hydrogen sulfide ammonia | 27 16 20 | 2 0 5 | 0 0 0 |

55 EXAMPLE A-14;

50 % hypophosphorous acid aqueous solution were added to 50 g of active carbon powder and mixed, where 25 g of calcium peroxide were added. After mixing uniformly, the mixture was dried at 110° C to

obtain a deodorant. The activity of the deodorant was measured in the same manner as in Example A-1. The results are shown in Table A-4.

EXAMPLES A-15 and A-16:

In the same manner as in Example A-14 except that 50 % phosphorous acid aqueous solution (Example A-15) and 50 % phosphoric acid aqueous solution (Example A-16) were used instead of 50 % hypophosphorous acid aqueous solution, the deodorants having the compositions shown in Table A-4 were obtained, respectively.

The activity of each of the deodorants was measured in the same manner as in Example A-1 and the results are shown in Table A-4.

EXAMPLES A-17;

In the same manner as in Example A-14, the deodorants having the compositions shown in Table A-4 were obtained, respectively and the activity of each of the deodorants was measured in the same manner as in Example A-1. The results are shown in Table A-4.

Table A-4

| Example | Composition | Substance | Concentration (ppm) after | | |
|---------|--------------------------------|------------------|---------------------------|--------|--------|
| | | | 15 min | 30 min | 60 min |
| A-14 | H_3PO_2/CaO_2 /active carbon | methylmercaptan | 25 | 7 | 0 |
| | | hydrogen sulfide | 10 | 3 | 0 |
| | | ammonia | 30 | 10 | 0 |
| A-15 | H_3PO_3/CaO_2 /active carbon | methylmercaptan | 30 | 10 | 0 |
| | | hydrogen sulfide | 15 | 5 | 0 |
| | | ammonia | 35 | 12 | 0 |
| A-16 | H_3PO_4/CaO_2 /active carbon | methylmercaptan | 28 | 7 | 0 |
| | | hydrogen sulfide | 15 | 5 | 0 |
| | | ammonia | 32 | 10 | 0 |
| A-17 | $FePO_4/BaO_2$ /silica-alumina | methylmercaptan | 45 | 15 | 0 |
| | | hydrogen sulfide | 25 | 8 | 0 |
| | | ammonia | 40 | 13 | 0 |

EXAMPLE 18;

In the same manner as in Example A-1 to A-6 except that phosphoric acid, phosphorous acid, sodium phosphate, sodium phosphite or sodium hypophosphite was used instead of hypophosphorous acid in Examples A-1 to A-6, the deodorants were obtained and the activity of each of the deodorants was

measured in the same manner as in Example A-1. Almost same results were obtained as those of Examples A-1 to A-6.

EXAMPLE A-19:

10 g of the deodorant prepared in Example A-7 were packed in a paper bag and three bags prepared above were placed in three different places in a public toilet of an area of 15 m². As a result, the so-called odor of the toilet was removed and the effect of the deodorant did not change after 3 months.

EXAMPLE A-20:

After packing 10 g of the deodorant prepared in Example A-7 in a paper bag, it was fixed on the inside of the cover of a polyethylene bucket of a capacity of 30 l containing raw garbage. As the result, the bad odor of the raw garbage was removed and the effect did not change after one month.

EXAMPLE A-21:

In the presence of a small amount of water, 25 g of calcium hypochlorite, 25 g of ferrous oxide and 50 g of granular silicaalumina (containing 28 % by weight of alumina) were kneaded to mix uniformly, and after drying the mixture at 110 °C, the obtained solid material was pulverized into powder of 16 to 24 mesh to obtain a deodorant.

After sealing 1 g of the thus obtained deodorant in a polyethylene vessel together with 500 ml of a sample gas containing 1000 ppm of methylmercaptan, 500 ppm of hydrogen sulfide and 1000 ppm of ammonia, the change of the concentration of each of the components in the vessel was measured. The results are shown in Table A-5.

EXAMPLES A-22 to A-23:

In the same manner as in Example A-21, the deodorants having the compositions shown in Table A-5 were obtained, respectively. The activity of the deodorants was measured and the results are also shown in Table A-5.

Table A-5

| Example | Composition | Substance | Concentration (ppm) after | | |
|---------|---|------------------|---------------------------|--------|---------|
| | | | 30 min | 1 hour | 2 hours |
| A-21 | Ca(ClO) ₂ /FeO/silica-alumina | methylmercaptan | 20 | 2 | 0 |
| | | hydrogen sulfide | 15 | 0 | 0 |
| | | ammonia | 15 | 0 | 0 |
| A-22 | Ca(ClO) ₂ /CoO/silica-alumina | methylmercaptan | 15 | 0 | 0 |
| | | hydrogen sulfide | 11 | 0 | 0 |
| | | ammonia | 10 | 0 | 0 |
| A-23 | Ca(ClO) ₂ /TiO ₂ /mordenite | methylmercaptan | 22 | 0 | 0 |
| | | hydrogen sulfide | 16 | 0 | 0 |
| | | ammonia | 20 | 0 | 0 |

55 EXAMPLES A-24

In the same manner as in Example A-21, the deodorants having the compositions shown in Table A-6 were obtained, respectively. The activity of each of the deodorants was measured in the same manner as in

Example A-21 and the results are shown in Table A-6.

EXAMPLE A-25:

5 In the presence of a small amount of water, 20 g of calcium hypochlorite, 20 g of ferrous oxide, 10 g of zinc oxide and 50 g of granular silica-alumina (containing 28 % by weight of alumina) were kneaded to mix uniformly, and after drying the mixture at 110 °C, the obtained solid material was pulverized into powder of 16 to 24 meshes to obtain a deodorant.

10 The activity of the deodorant was measured in the same manner as in Example A-21 and the results are shown in Table A-7.

EXAMPLE A-26

15 In the same manner as in Example A-25, the deodorants having the compositions shown in Table A-7 were obtained, respectively. The activity of each of the deodorants was measured and the results are also shown in Table A-7.

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Table A-6

| Example | Composition | Substance | Concentration (ppm) after | | |
|---------|-------------------------|--|---------------------------|--------|---------|
| | | | 30 min | 1 hour | 2 hours |
| A-24 | NaClO/CuO/active carbon | methylmercaptan hydrogen sulfide ammonia | 30 | 2 | 0 |
| | | | 15 | 0 | 0 |
| | | | 20 | 1 | 0 |

Table A-7

| Example | Composition | Substance | Concentration (ppm) after | | |
|---------|---|--|---------------------------|--------|---------|
| | | | 30 min | 1 hour | 2 hours |
| A-25 | Ca(ClO) ₂ /FeO/ZnO/Silica-alumina | methylmercaptan hydrogen sulfide ammonia | 16 | 0 | 0 |
| | | | 10 | 0 | 0 |
| | | | 12 | 0 | 0 |
| A-26 | Ca(ClO) ₂ /FeO/CaO/ active carbon | methylmercaptan hydrogen sulfide ammonia | 15 | 0 | 0 |
| | | | 7 | 0 | 0 |
| | | | 10 | 0 | 0 |

In Table A-7, the composition ratio is 20/20/10/50 (by weight) in Examples A-25 and A-26.

EXAMPLE A-27:

In the presence of a small amount of water, 25 g of calcium hypochlorite, 25 g of zinc oxide and 50 g of granular silicaalumina (containing 28 % by weight of alumina) were kneaded to mix uniformly and after

drying the mixture at 110°C the obtained solid material was pulverized into powder of 1,0 to 0,70 mm (16 to 24 meshes) to obtain a deodorant.

After sealing 1 g of the deodorant in a polyethylene vessel together with 500 ml of a sample gas containing 1000 ppm of methylmercaptan, 500 ppm of hydrogen sulfide and 1000 ppm of ammonia, the change of the concentration of each of the components was measured. The results are shown in Table A-8.

EXAMPLES A-28 to A-30:

Example A-27 was repeated except that magnesium oxide (Example A-28) calcium oxide (Example A-29), and barium oxide (Example A-30) were used respectively instead of zinc oxide to obtain the deodorants shown in Table A-8. The activity of each of the deodorants was measured and the results are also shown in Table A-8.

EXAMPLE A-31:

136.4 g of barium nitrate and 146.2 g of zinc nitrate were dissolved into 800 ml of water, where 200 g of silica-alumina were added. After evaporating the mixture to dryness under agitation, the obtained solid material was pulverized into powder of 1,0 to 0,70 m 16 to 24 meshes and then calcined for 4 hours at 500°C. The composition of the solid material obtained was BaO : ZnO : silica-alumina = 20 :10 : 50 (by weight).

200 ml of 10 % calcium hypochlorite aqueous solution were added to 80 g of the solid material obtained above and the mixture was evaporated to dryness and dried at 110°C to obtain a deodorant.

After sealing 1 g of the deodorant in a polyethylene vessel together with 500 ml of a sample gas containing 11000 ppm of methylmercaptan, the change of the concentration of methylmercaptan was measured. The results are shown in Table A-9.

COMPARATIVE EXAMPLE:

A test was carried out in the same manner as in Example A-31 while using the composition shown in Table A-9 and the test results are shown in Table A-9.

EXAMPLE A-32 A-:

In the same manner as in Example A-31, the deodorants having the compositions shown in Table A-10 were prepared, and the activity of each of the deodorants was measured in the same manner as in Example A-27. The results are shown in Table A-10.

Table A-8

| Example | Composition | Substance | Concentration (ppm) after | | |
|---------|---|--|---------------------------|-------------|-------------|
| | | | 30 min | 1 hour | 2 hours |
| A-27 | $\text{Ca}(\text{ClO})_2/\text{ZnO/silica-alumina}$ | methylmercaptan hydrogen sulfide ammonia | 25 10 15 | 2 1 2 | 0 0 0 |
| A-28 | $\text{Ca}(\text{ClO})_2/\text{MgO/silica-alumina}$ | methylmercaptan hydrogen sulfide ammonia | 38 25 25 | 4 5 4 | 0 0 0 |
| A-29 | $\text{Ca}(\text{ClO})_2/\text{CaO/silica-alumina}$ | methylmercaptan hydrogen sulfide ammonia | 35 22 27 | 4 4 5 | 0 0 0 |
| A-30 | $\text{Ca}(\text{ClO})_2/\text{NaO/silica-alumina}$ | methylmercaptan hydrogen sulfide ammonia | 45 35 50 | 5 3 7 | 0 0 0 |

Table A-9

| | Composition | Concentration of methylmercaptan(ppm) after | | |
|---------------------|--|---|--------|---------|
| | | 30 min. | 1 hour | 2 hours |
| Example A-31 | Ca(C10) ₂ /BaO/ZnO/silica-alumina | 150 | 12 | 0 |
| Comparative Example | Ca(C10) ₂ | 7700 | 7975 | 7560 |
| | silica-alumina | 9680 | 9570 | 9500 |
| | BaO/ZnO/silica-alumina | 8910 | 8800 | 8820 |

Table A-10

| Example | Composition | Substance | Concentration (ppm) after | | |
|---------|--|--|---------------------------|--------|---------|
| | | | 30 mm | 1 hour | 2 hours |
| A-32 | Ba (ClO) ₂ /CaO/ZnO/ Na ⁺ zeolite | methylmercaptan hydrogen sulfide ammonia | 60 | 10 | 0 |
| | | | 45 | 2 | 0 |
| | | | 52 | 7 | 0 |

55 EXAMPLES A-33 and A-34:

100 g of dehydrated sewage sludge were placed into a glass bottle of 2 l in capacity and covered with 2 g of the deodorants prepared in Example A-7 and A-13, respectively.

After the closely sealed bottle was allowed to stand for 24 hours at 30°C, the concentrations of methylmercaptan and hydrogen sulfide were measured.

As a result, they were 200 ppm and 100 ppm, respectively, in the test without the deodorants, while the concentrations of both compounds were less than 1 ppm in each test.

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Claims

1. A method for adsorbing and decomposing ethylene and/or other odorous substances present in air or other odor-generating sources,
 10 which method comprises placing in proximity to said source a composition which comprises
 (A) at least one compound selected from the group consisting of phosphoric acid, phosphorous acid, hypophosphorous acid, salts of said acids and hypochlorite and
 (B) at least one compound selected from the group consisting of oxides and peroxides of iron, cobalt, titanium, copper, zinc, magnesium, calcium, and barium,
 15 the weight ratio of the component (A) to the component (B) being in the range of 1 : 0.001-99.
2. The method according to claim 1 for removing ethylene from an ethylene-generating source, which method comprises placing in proximity to said source a composition which comprises
 (A) at least one compound selected from the group consisting of phosphoric acid, phosphorous acid, hypophosphorous acid, salts of said acids and hypochlorite and
 20 (B) at least one compound selected from the group consisting of oxides and peroxides of cobalt, titanium, copper, zinc, magnesium, calcium and barium, and Fe_2O_3 ,
 the weight ratio of the component (A) to the component (B) being in the range of 1 : 0.001-99.
- 25 3. The method according to claim 1 for preserving harvested fruits, vegetables or flowers, which method comprises placing in proximity to said fruits, vegetables or flowers a composition which comprises
 (A) at least one compound selected from the group consisting of phosphoric acid, phosphorous acid, hypophosphorous acid, salts of said acids and hypochlorite and
 30 (B) at least one compound selected from the group consisting of oxides and peroxides of cobalt, titanium, copper, zinc, magnesium, calcium and barium, and Fe_2O_3 ,
 the weight ratio of the component (A) to the component (B) being in the range of 1 : 0.001-99.
- 35 4. The method according to claim 1 for deodorizing a gas which comprises odorous substances, which method comprises bringing said gas into contact with a composition which comprises
 (A) at least one compound selected from the group consisting of phosphoric acid, phosphorous acid, hypophosphorous acid and hypochlorite and
 (B) at least one compound selected from the group consisting of oxides and peroxides of iron, titanium, copper, zinc, magnesium, calcium and barium,
 40 the weight ratio of the component (A) to the component (B) being in the range of 1 : 0.001-99.
5. The method according to claim 1 for deodorizing an odorgenerating source, which method comprises adding to said source a composition which comprises
 (A) at least one compound selected from the group consisting of phosphoric acid, phosphorous acid, hypophosphorous acid and hypochlorite and
 45 (B) at least one compound selected from the group consisting of oxides and peroxides of iron, titanium, copper, zinc, magnesium, calcium and barium,
 the weight ratio of the component (A) to the component (B) being in the range of 1 : 0.001 - 99.
- 50 6. The method according to any of claims 1 to 5, wherein the weight ratio of the component (A) to the component (B) is in the range of 1 : 0.001-30.
7. The method according to claim 2 or 3, wherein the component (A) is at least one compound selected from the group consisting of phosphoric acid, hypophosphorous acid and calcium hypochlorite.
- 55 8. The method according to claim 2 or 3, wherein the component (B) is at least one compound selected from the group consisting of oxides or peroxides of titanium, copper, zinc, magnesium, calcium and barium, and Fe_2O_3 .

9. The method according to claim 8, wherein the component (B) is at least one compound selected from the group consisting of Fe_2O_3 , zinc oxide and calcium peroxide.
10. The method according to claim 2 or 3, wherein the component (A) is at least one compound selected from the group consisting of phosphoric acid, hypophosphorous acid and calcium hypochlorite and the component (B) is at least one compound selected from the group consisting of oxides or peroxides of titanium, copper, zinc, magnesium, calcium and barium, and Fe_2O_3 .
11. The method according to claim 10, wherein the component (B) is at least one compound selected from the group consisting of Fe_2O_3 , zinc oxide and calcium peroxide.
12. The method according to claim 4 or 5, wherein the component (A) is phosphoric acid.
13. The method according to claim 4 or 5, wherein the component (B) is at least one compound selected from the group consisting of Fe_2O_3 , titanium oxide and calcium peroxide.
14. The method according to claim 4 or 5, wherein the component (A) is phosphoric acid and the component (B) is at least one compound selected from the group consisting of oxides and peroxides of iron, titanium, copper, zinc, magnesium, calcium and barium.
15. The method according to claim 14, wherein the component (B) is at least one compound selected from the group consisting of Fe_2O_3 , titanium oxide and calcium peroxide.
16. The method according to any of claims 1 to 15, wherein the component (A) and the component (B) have been carried on a carrier.
17. The method according to claim 16, wherein said carrier is at least one carrier selected from the group consisting of silica, alumina, silica-alumina, natural zeolite, synthetic zeolite, diatomaceous earth, Kanuma earth, clays and active carbon.

Patentansprüche

1. Verfahren zum Adsorbieren und Zersetzen von Ethylen und/oder anderen in Luft oder anderen geruchserzeugenden Quellen vorliegenden Geruchssubstanzen, wobei das Verfahren umfaßt, daß in die Nähe der Quelle eine Zusammensetzung gebracht wird, die umfaßt:
 - (A) mindestens eine Verbindung ausgewählt aus der Gruppe bestehend aus Phosphorsäure, phosphoriger Säure, unterphosphoriger Säure, Salzen dieser Säuren und Hypochlorit und
 - (B) mindestens eine Verbindung ausgewählt aus der Gruppe bestehend aus Oxiden und Peroxiden von Eisen, Kobalt, Titan, Kupfer, Zink, Magnesium, Calcium und Barium,
 wobei das Gewichtsverhältnis der Komponente (A) zu der Komponente (B) in dem Bereich von 1 : 0,001-99 liegt.
2. Verfahren nach Anspruch 1 zum Entfernen von Ethylen aus einer Ethylen erzeugenden Quelle, wobei das Verfahren umfaßt, daß in die Nähe der Quelle eine Zusammensetzung gebracht wird, die umfaßt:
 - (A) mindestens eine Verbindung ausgewählt aus der Gruppe bestehend aus Phosphorsäure, phosphoriger Säure, unterphosphoriger Säure, Salzen dieser Säuren und Hypochlorit und
 - (B) mindestens eine Verbindung ausgewählt aus der Gruppe bestehend aus Oxiden und Peroxiden von Kobalt, Titan, Kupfer, Zink, Magnesium, Calcium und Barium, sowie Fe_2O_3 ,
 wobei das Gewichtsverhältnis der Komponente (A) zu der Komponente (B) in dem Bereich von 1 : 0,001-99 liegt.
3. Verfahren nach Anspruch 1 zum Konservieren geernteter Früchte, Gemüse oder Blumen, wobei das Verfahren umfaßt, daß in die Nähe der Früchte, des Gemüse oder der Blumen eine Zusammensetzung gebracht wird, die umfaßt:
 - (A) mindestens eine Verbindung ausgewählt aus der Gruppe bestehend aus Phosphorsäure, phosphoriger Säure, unterphosphoriger Säure, Salzen dieser Säuren und Hypochlorit und
 - (B) mindestens eine Verbindung ausgewählt aus der Gruppe bestehend aus Oxiden und Peroxiden von Kobalt, Titan, Kupfer, Zink, Magnesium, Calcium und Barium, sowie Fe_2O_3 ,

wobei das Gewichtsverhältnis der Komponente (A) zu der Komponente (B) in dem Bereich von 1 : 0,001-99 liegt.

4. Verfahren nach Anspruch 1 zum Desodorieren eines Gases, das Geruchssubstanzen umfaßt, wobei das Verfahren umfaßt, daß das Gas mit einer Zusammensetzung in Kontakt gebracht wird, die umfaßt:
 - (A) mindestens eine Verbindung ausgewählt aus der Gruppe bestehend aus Phosphorsäure, phosphoriger Säure, unterphosphoriger Säure und Hypochlorit und
 - (B) mindestens eine Verbindung, ausgewählt aus der Gruppe bestehend aus Oxiden und Peroxiden von Eisen, Titan, Kupfer, Zink, Magnesium, Calcium und Barium,
 wobei das Gewichtsverhältnis der Komponente (A) zu der Komponente (B) in dem Bereich von 1 : 0,001-99 liegt.
5. Verfahren nach Anspruch 1 zum Desodorieren einer geruchserzeugenden Quelle, wobei das Verfahren umfaßt, daß der Quelle eine Zusammensetzung zugegeben wird, die umfaßt
 - (A) mindestens eine Verbindung ausgewählt aus der Gruppe bestehend aus Phosphorsäure, phosphoriger Säure, unterphosphoriger Säure und Hypochlorit und
 - (B) mindestens eine Verbindung, ausgewählt aus der Gruppe bestehend aus Oxiden und Peroxiden von Eisen, Titan, Kupfer, Zink, Magnesium, Calcium und Barium,
 wobei das Gewichtsverhältnis der Komponente (A) zu der Komponente (B) in dem Bereich von 1 : 0,001-99 liegt.
6. Verfahren nach einem der Ansprüche 1 bis 5, wobei das Gewichtsverhältnis der Komponente (A) zu der Komponente (B) im Bereich von 1:0,001-30 liegt.
7. Verfahren nach Anspruch 2 oder 3, wobei die Komponente (A) mindestens eine Verbindung ausgewählt aus der Gruppe bestehend aus Phosphorsäure, unterphosphoriger Säure und Calciumhypochlorit ist.
8. Verfahren nach Anspruch 2 oder 3, wobei die Komponente (B) mindestens eine Verbindung ausgewählt aus der Gruppe bestehend aus Oxiden und Peroxiden von Titan, Kupfer, Zink, Magnesium, Calcium und Barium, sowie Fe_2O_3 ist.
9. Verfahren nach Anspruch 8, wobei die Komponente (B) mindestens eine Verbindung ausgewählt aus der Gruppe bestehend aus Fe_2O_3 , Zinkoxid und Calciumperoxid ist.
10. Verfahren nach Anspruch 2 oder 3, wobei die Komponente (A) mindestens eine Verbindung ausgewählt aus der Gruppe bestehend aus Phosphorsäure, unterphosphoriger Säure und Calciumhypochlorit ist und die Komponente (B) mindestens eine Verbindung ausgewählt aus der Gruppe bestehend aus Oxiden und Peroxiden von Titan, Kupfer, Zink, Magnesium, Calcium und Barium, sowie Fe_2O_3 ist.
11. Verfahren nach Anspruch 10, wobei die Komponente (B) mindestens eine Verbindung ausgewählt aus der Gruppe bestehend aus Fe_2O_3 , Zinkoxid und Calciumperoxid ist.
12. Verfahren nach Anspruch 4 oder 5, wobei die Komponente (A) Phosphorsäure ist.
13. Verfahren nach Anspruch 4 oder 5, wobei die Komponente (B) mindestens eine Verbindung ausgewählt aus der Gruppe bestehend als Fe_2O_3 , Titanoxid und Calciumperoxid ist.
14. Verfahren nach Anspruch 4 oder 5, wobei die Komponente (A) Phosphorsäure und die Komponente (B) mindestens eine Verbindung ausgewählt aus der Gruppe bestehend aus Oxiden und Peroxiden von Eisen, Titan, Kupfer, Zink, Magnesium, Calcium und Barium ist.
15. Verfahren nach Anspruch 14, worin die Komponente (B) mindestens eine Verbindung ausgewählt aus der Gruppe bestehend aus Fe_2O_3 , Titanoxid und Calciumperoxid ist.
16. Verfahren nach einem der Ansprüche 1 bis 15, worin die Komponente (A) und die Komponente (B) von einem Träger getragen werden.

17. Verfahren nach Anspruch 16, worin der Träger mindestens ein Träger ausgewählt aus der Gruppe bestehend aus Siliziumdioxid, Aluminiumoxid, Siliziumdioxid-Aluminiumoxid, natürlichem Zeolith, synthetischem Zeolith, Kieselgur, Kanuma-Erde, Tone und Aktivkohle ist.

5 Revendications

1. Procédé pour adsorber et décomposer l'éthylène et/ou d'autres substances odorantes présentes dans l'air ou d'autres sources génératrices d'odeur, lequel procédé consiste à placer à proximité de ladite source une composition qui comprend
 - (A) au moins un composé choisi dans le groupe formé par l'acide phosphorique, l'acide phosphoreux, l'acide hypophosphoreux, les sels desdits acides et un hypochlorite, et
 - (B) au moins un composé choisi dans le groupe formé par les oxydes et peroxydes de fer, cobalt, titane, cuivre, zinc, magnésium, calcium et baryum,
 le rapport en poids du composant (A) au composant (B) étant compris dans l'intervalle de 1:0,001 à 1:99.
2. Procédé selon la revendication 1 pour éliminer l'éthylène d'une source génératrice d'éthylène, lequel procédé consiste à placer à proximité de ladite source une composition qui comprend
 - (A) au moins un composé choisi dans le groupe formé par l'acide phosphorique, l'acide phosphoreux, l'acide hypophosphoreux, les sels desdits acides et un hypochlorite, et
 - (B) au moins un composé choisi dans le groupe formé par les oxydes et peroxydes de cobalt, titane, cuivre, zinc, magnésium, calcium et baryum, et Fe_2O_3 ,
 le rapport en poids du composant (A) au composant (B) étant compris dans l'intervalle de 1:0,001 à 1:99.
3. Procédé selon la revendication 1 pour conserver des fruits, légumes ou fleurs récoltés, lequel procédé consiste à placer à proximité desdits fruits, légumes ou fleurs une composition qui comprend
 - (A) au moins un composé choisi dans le groupe formé par l'acide phosphorique, l'acide phosphoreux, l'acide hypophosphoreux, les sels desdits acides et un hypochlorite, et
 - (B) au moins un composé choisi dans le groupe formé par les oxydes et peroxydes de cobalt, titane, cuivre, zinc, magnésium, calcium et baryum, et Fe_2O_3 ,
 le rapport en poids du composant (A) au composant (B) étant compris dans l'intervalle de 1:0,001 à 1:99.
4. Procédé selon la revendication 1 pour désodoriser un gaz qui contient des substances odorantes, lequel procédé consiste à mettre ledit gaz en contact avec une composition qui comprend
 - (A) au moins un composé choisi dans le groupe formé par l'acide phosphorique, l'acide phosphoreux, l'acide hypophosphoreux et un hypochlorite, et
 - (B) au moins un composé choisi dans le groupe formé par les oxydes et peroxydes de fer, titane, cuivre, zinc, magnésium, calcium et baryum,
 le rapport en poids du composant (A) au composant (B) étant compris dans l'intervalle de 1:0,001 à 1:99.
5. Procédé selon la revendication 1 pour désodoriser une source génératrice d'odeur, lequel procédé consiste à ajouter à ladite source une composition qui comprend
 - (A) au moins un composé choisi dans le groupe formé par l'acide phosphorique, l'acide phosphoreux, l'acide hypophosphoreux et un hypochlorite, et
 - (B) au moins un composé choisi dans le groupe formé par les oxydes et peroxydes de fer, titane, cuivre, zinc, magnésium, calcium et baryum,
 le rapport en poids du composant (A) au composant (B) étant compris dans l'intervalle de 1:0,001 à 1:99.
6. Procédé selon l'une quelconque des revendications 1 à 5, dans lequel le rapport en poids du composant (A) au composant (a) est compris dans l'intervalle de 1:0,001 à 1:30.
7. Procédé selon la revendication 2 ou 3, dans lequel le composant (A) est au moins un composé choisi dans le groupe formé par l'acide phosphorique, l'acide hypophosphoreux et l'hypochlorite de calcium.

8. Procédé selon la revendication 2 ou 3, dans lequel le composant (B) est au moins un composé choisi dans le groupe formé par les oxydes et peroxydes de titane, cuivre, zinc, magnésium, calcium et baryum, et Fe_2O_3 .
- 5 9. Procédé selon la revendication 8, dans lequel le composant (B) est au moins un composé choisi dans le groupe formé par Fe_2O_3 , l'oxyde de zinc et le peroxyde de calcium.
- 10 10. Procédé selon la revendication 2 ou 3, dans lequel le composant (A) est au moins un composé choisi dans le groupe formé par l'acide phosphorique, l'acide hypophosphoreux et l'hypochlorite de calcium, et le composant (B) est au moins un composé choisi dans le groupe formé par les oxydes et peroxydes de titane, cuivre, zinc, magnésium, calcium et baryum, et Fe_2O_3 .
11. Procédé selon la revendication 10, dans lequel le composant (B) est au moins un composé choisi dans le groupe formé par Fe_2O_3 , l'oxyde de zinc et le peroxyde de calcium.
- 15 12. Procédé selon la revendication 4 ou 5, dans lequel le composant (A) est l'acide phosphorique.
13. Procédé selon la revendication 4 ou 5, dans lequel le composant (B) est au moins un composé choisi dans le groupe formé par Fe_2O_3 , l'oxyde de titane et le peroxyde de calcium.
- 20 14. Procédé selon la revendication 4 ou 5, dans lequel le composant (A) est l'acide phosphorique et le composant (a) est au moins un composé choisi dans le groupe formé par les oxydes et peroxydes de fer, titane, cuivre, zinc, magnésium, calcium et baryum.
- 25 15. Procédé selon la revendication 14, dans lequel le composant (B) est au moins un composé choisi dans le groupe formé par Fe_2O_3 , l'oxyde de titane et le peroxyde de calcium.
16. Procédé selon l'une quelconque des revendications 1 à 15, dans lequel le composant (A) et le composant (B) ont été déposés sur un support.
- 30 17. Procédé selon la revendication 16, dans lequel ledit support est au moins un support choisi dans le groupe formé par la silice, l'alumine, une silice-alumine, une zéolite naturelle, une zéolite synthétique, la terre de diatomées, la terre de Kanuma, les argiles et le charbon actif.